

**INVESTIGATING THE USE OF CHELATING AGENTS FOR CLAY
DISSOLUTION AND SANDSTONE ACIDIZING PURPOSES**

A Thesis

by

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ABSTRACT

Mud acid, a mixture of HCl and HF, has been frequently used for stimulating sandstone reservoirs. However, using HCl in such environments can be problematic, especially at higher temperatures. Some of the most common problems are the following: clay sensitivity, secondary/tertiary reactions, and precipitation of salts and corrosion. To combat these problems mixtures of HF have been developed along with organic acids and chelating agents such as citric acid, acetic acid, EDTA, HEDTA, GLDA etc. Compared to HCl, these chelating agents offer lower corrosion, no mineral sensitivity issues, stability at high temperatures (< 200 °F) and bio-degradability.

This thesis explores the use of two chelating agents, citric acid and a newly developed sodium salt of L-Glutamic acid N,N-Di Acetic Acid (Na-GLDA). Experiments were conducted to find out the aluminosilicates dissolution and chelation capabilities of these chelating agents. The first set of experiments were clay dissolution experiments, conducted using different concentrations of citric acid (1 wt%, 3 wt%, and 5 wt%) added to regular 9:1 mud acid. This was done to study and analyze its clay dissolution properties, as well as its chelation abilities to reduce precipitation. For comparison purposes, experiments were also completed using regular 9:1 mud acid to compare its results to that of using citric acid along with 9:1 mud acid. The results suggest that using 1 wt% citric acid along with 9:1 mud acid provided the best results, both in terms of clay dissolution as well as reducing precipitate formation.

The next set of experiments investigated the use of Na-GLDA along with HF for sandstone acidizing purposes. First, compatibility experiments were conducted to find out the optimum acid mixture between Na-GLDA and HF that causes no incompatibilities. Following the compatibility test, coreflood experiments were run on Bandera and Berea cores using the optimum acid mixture formulation found in the preceding experiment. Coreflood results showed the good chelation ability of Na-GLDA to iron, calcium and magnesium. But very low concentrations of any aluminosilicates were found in the ICP samples indicating either the lack of dissolution of aluminosilicates or the precipitation of aluminosilicates within the core.

In conclusion, the experimental results suggest that adding 1 wt% citric acid to 9:1 mud acid provides better dissolution and precipitation results. But factoring in the cost of citric acid makes it a financially unfavorable formulation, especially since regular 9:1 mud acid performed almost as well as 9:1 mud acid with 1 wt% citric acid added to it. Also, the newly developed Na-GLDA is compatible with HF at certain concentrations of both. The optimum acid mixture formulation was found to be 20 wt% Na-GLDA + 1 wt% HF. Coreflood results show that Na-GLDA added to HF is able to keep cations such as iron, calcium and magnesium in solution at higher temperatures, but it is unable to properly dissolve and chelate to aluminosilicates and its damaging salts.

DEDICATION

I dedicate this work to my parents, my family and friends.

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CHAPTER I

INTRODUCTION

Background

The main goal of sandstone acidizing is to remove formation damage within the matrix caused by fines migration, clay swelling, and mineral incompatibilities due to drilling or completion fluids. These damaging components are usually aluminosilicates and clays, which must be removed using HF. However, in order to maintain an acidic environment and to prevent additional reactions, HCl is added to reduce the pH (Yang et al. 2012). The most common formulation used for sandstone acidizing purposes is called mud acid, which consists of HCl and HF, usually in weight percent ratios of 12 wt% HCl to 3 wt% HF or 9 wt% HCl to 1wt% HF. Even though mud acid is a commonly used acid formulation, it does have major drawbacks including clay sensitivity, corrosion and rapid spending of HF/HCl to form damaging precipitates.

HCl is corrosive especially at high temperature and can cause several problems due to corrosion. Therefore, instead of HCl, organic acids are used. The mixture of HF and organic acid that is used as the main stage in acidizing sandstone reservoirs is known as organic mud acid. HCl will also be replaced by a mixture of HCl and formic acid to avoid corrosion. Ammonium chloride is used as a preflush to replace sodium and potassium cations to avoid precipitation of fluosilicate salts (Gdanski 1998). The injection of HCl into sandstone reservoirs with illite and chlorite clays can pose another problem, as they are HCl sensitive and result in fines migration, which leads to severe

formation damage (Thomas et al. 2001). HCl use in certain sandstone reservoirs can also cause precipitation of amorphous silica gel, as aluminum is preferentially leached of silicon from kaolinite clays (Bryant and Buller 1990). This in turn causes fines migration within the core, causing further problems.

Organic acid based formulations of HF have been studied using acetic acid, formic acid and citric acid. They have their limitations though, such as susceptibility to harmful salt precipitation and incomplete reactions due to equilibrium factors. Retarded HF systems have also been tested extensively, but problems have been found using them as well due to precipitation of damaging salts and marginal reaction rate reduction.

Chelating agents, also known as complexing or sequestering agents, are compounds that form stable complexes with divalent and trivalent cations. They achieve this by coordinating with ions at multiple sites. For the purpose of acidizing, these chelating agents act like claws which hook onto specific metal ions in solution, binding to them, thus not allowing them to precipitate out of solution and cause formation damage. These chelating agents also serve as secondary acids as they help dissolve calcium from the matrix and prevent precipitation of calcium fluorides. Some of the major advantages to using chelating agents over HCl are as follows: reduced corrosion, precipitation control, no clay sensitivity, biodegradability, and thermal stability.

Citric acid has typically been used to control free iron cations in spent HCl solutions by chelating to iron and preventing the precipitation of iron hydroxide or iron sulfide. Citric acid is also a weak acid, so it does not react very strongly with the matrix as compared to HF. It is also more thermally stable than HCl, and can thus be used for

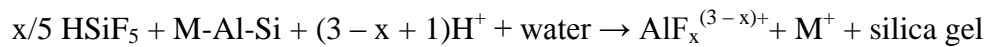
higher temperature applications as well. L-glutamic acid N,N-diacetic acid or GLDA has been recently developed by AkzoNobel for acidizing purposes in carbonate reservoirs, and currently its application into sandstone reservoirs is being studied as well. GLDA improves on the limitations of other chelating agents such as EDTA, NTA and HEDTA, which had poor ecological and toxicological profiles making them difficult to handle. GLDA is environmentally friendly and non-toxic, and it has better solubility across a wider pH range. It is also thermally stable at higher temperatures.

In order to study the use of acidizing formulations for sandstone acidizing purposes, understanding the various reactions and problems is required. Sandstone acidizing is a complicated process involving many variables that have the potential to cause harm. In order to sustain a successful acidizing job, control of free cations and minimization of precipitations is important (Gdanski 1999). The most important chemical interactions are those between the acid mixture and aluminosilicates or clays. The reaction of clays with HF acid is very complex. The interactions happen in three stages: primary reactions, secondary reactions, and tertiary reactions.

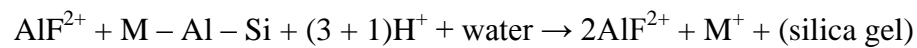
The primary reaction is mass-transfer dominated and rates increase rapidly at higher temperatures. The primary reaction involves the interaction of HF with sand (SiO_2) and aluminosilicates to form fluosilicic acid and aluminum fluoride salts (Gdanski 2000). The reaction is shown below:



In the above reaction, x is the number of fluoride atoms needed to dissolve one atom of aluminum and M is any metal cation. A huge majority of the permeability enhancement and formation damage removal is achieved by this reaction (Gdanski 1999). The secondary reaction proceeds at temperatures over 125°F, and it involves the reaction of fluosilicic acid with aluminosilicates. This reaction leads to the formation of more aluminum fluoride species and silica gel. The reaction is shown below:



The tertiary reaction involves the reaction between the aluminum fluoride species and aluminosilicates to extract the aluminum out of the aluminosilicate and reduce it to a silica gel-like precipitate. The reaction is shown below (Shuchart and Buster 1995):



Understanding these three reactions mentioned above is critical to designing the right acid formation. One of the most important reasons for studying chelating agents is that they minimize free cations in solution, thus not allowing secondary and tertiary reactions to proceed especially at higher temperatures.

Literature Review

The use of organic acids such as citric acid has been studied extensively to treat sandstone and carbonate reservoirs. They have been preferred over mud acid due to their

retarded nature, low corrosion rates and thermal stability (Shuchart and Gdanski 1996). The use of organic acid systems is even more prevalent in sandstone reservoirs contain acid sensitive clays such as illite, which facilitates fines migration when exposed to HCl. The most commonly used formulations of organic acids involve using acetic or formic acid along with HF. The concentrations are kept to prevent reaction product precipitation and financial costs. Wehunt et al. (1993) tested acetic acid, propanoic acid, and butanoic acid and found acetic acid to work the best amongst the three. Citric acid, unlike acetic acid and formic acid, has not been used as much for acidizing purposes, and very little experimental work has been done using it in sandstone reservoirs.

GLDA or L-glutamic acid N,N-diacetic acid is a novel bio-friendly chelating agent that is being tested in the field and laboratories for use with HF for high temperature acidizing purposes. Chelating agents such as GLDA, EDTA, and HEDTA, were first used to dissolve scale caused by sulfate and carbonate salts. These chelating agents are very adept at dissolving carbonates and chelating to cations free in solution, thus reducing any unnecessary precipitates and reducing the formation damage. HEDTA was the most commonly used chelating agent used with HF in recent years. It has been applied in the field to treat Berea cores (Parkinson et al. 2010), and the results showed a higher permeability gain compared to using regular 9:1 mud acid. These results match the work of Ali et al. (2002), which showed that HEDTA gave better permeability results compared to EDTA and regular mud acid formulations. With recent developments in chelate synthesis, GLDA was developed to overcome the shortcomings of HEDTA, which were poor biodegradability and poor thermal stability. To add to the list

of benefits, GLDA also has very high solubility in acidic solutions, so more chelating agent can be added for a given volume of the acid formulation. This can help reduce financial costs and reduce the amount of acid that has to be injected for each job.

Recent experiments have shown that GLDA performs much better than HEDTA, EDTA and mud acid for stimulating sandstone cores, yielding much higher return permeabilities along with greater aluminosilicate chelation and dissolution (Mahmoud et al. 2011). A recent study by LePage et al. (2011) has suggested that GLDA has the best chelation abilities with respect to calcium and iron cations, and it has the widest solubility range amongst all the chelating agents in use today. Mahmoud et al. (2011) used GLDA along with HF to stimulate Berea and Bandera cores, and results showed that GLDA was able to chelate free cations and increase core permeability.

Research Goals

In order to deal with the complexities of using mud acid in sandstone reservoirs effectively, novel chelating agents have been developed and tested. Primary concerns with new chemicals are the compatibility with HF, clay dissolution capabilities and precipitate mitigation ability. Citric acid and monosodium GLDA or Na-GLDA will be evaluated for use with HF in this paper. Listed below are the specific objectives for this thesis:

1. Study the dissolution of clays using citric acid based mud acid.
 - Run clay dissolution tests using 9:1 mud acid and compare it to citric acid based 9:1 mud acid solutions.

- Compare reaction residue and filtrate for dissolution and precipitate analysis.
2. Study the compatibility of Na-GLDA with HF for sandstone acidizing purposes.
 - Analyze the compatibility issues between Na-GLDA and HF at varying concentrations of each.
 - Develop an optimum acid mixture formulation for experimental use.
 - Use analytical techniques like SEM-EDS to identify the type of precipitate formed when certain mixtures of Na-GLDA and HF are formulated.
 3. Conduct coreflood analysis of sandstone cores using Na-GLDA and HF at 300°F.
 - Run coreflood experiments using the optimum acid mixture formulation for Na-GLDA and HF.
 - Analyze ICP samples and return permeability tests to evaluate stimulation success or failure.

CHAPTER II

MATERIALS AND METHODS

This section is divided into two sub-parts. The first part of the section will discuss the apparatus and chemicals used for the experiments. The second part of this section will briefly explain the methods used to run the experiments successfully.

Materials and Chemicals Used

Coreflood Apparatus

The coreflood setup was used to simulate a stimulation job in the field by creating an isolated area for stimulating agents to come into contact with a reservoir core of our choice. This setup can be approximated to run at steady state, which lets us use Darcy's Law to find out permeability if we know the flowrate and pressure drop. A back pressure of 1500 psi was applied to keep the carbon dioxide generated during calcium dissolution in solution. A pressure transducer installed on the coreflood setup relays the pressure drop across the core to a computer during the experiments. The transducer employed is an IDP-10 model manufactured by Foxboro Invensys, and its accuracy is 0.001% of the calibrated range of the transducer. Two different transducers were used to monitor the pressure drop, depending on which setup was used for each test. Their calibrated range is 1000 and 300 psi respectively. A Teledyne ISCO D-series D1000 precision syringe pump, that had a maximum allowable working pressure of 2000 psi, was used to inject fluids into the core sample. All the coreflood tests were run at a

temperature 300 °F using 6 inch Berea and Bandera sandstone core samples. The main acid used for all injections was 20 wt% Na-GLDA + 1 wt% HF. The pre-flush consisted of 5 wt% ammonium chloride and 20 wt% GLDA. The post-flush for all experiments was 5wt% ammonium chloride. In order to maintain the core at a constant temperature, two temperature controllers were used. The temperature of the preheated fluids coming from the accumulators was controlled by a compact bench top CSC32 series, which has a 4-digit display, a 0.1° resolution, uses a type K thermocouple and two outputs (5A 120 Vac SSR), and has an accuracy of $\pm 0.25\%$ full scale $\pm 1^{\circ}\text{C}$. LabView® software was used on the PC to monitor the pressure drop across the core sample during treatment. The LabView® data acquisition software was set up so as to collect a reading of the pressure difference between the core sample inlet and outlet once every five seconds. This data was used to develop pressure drop versus time graphs to help calculate permeability. Figure 1 is a schematic of the coreflood setup:

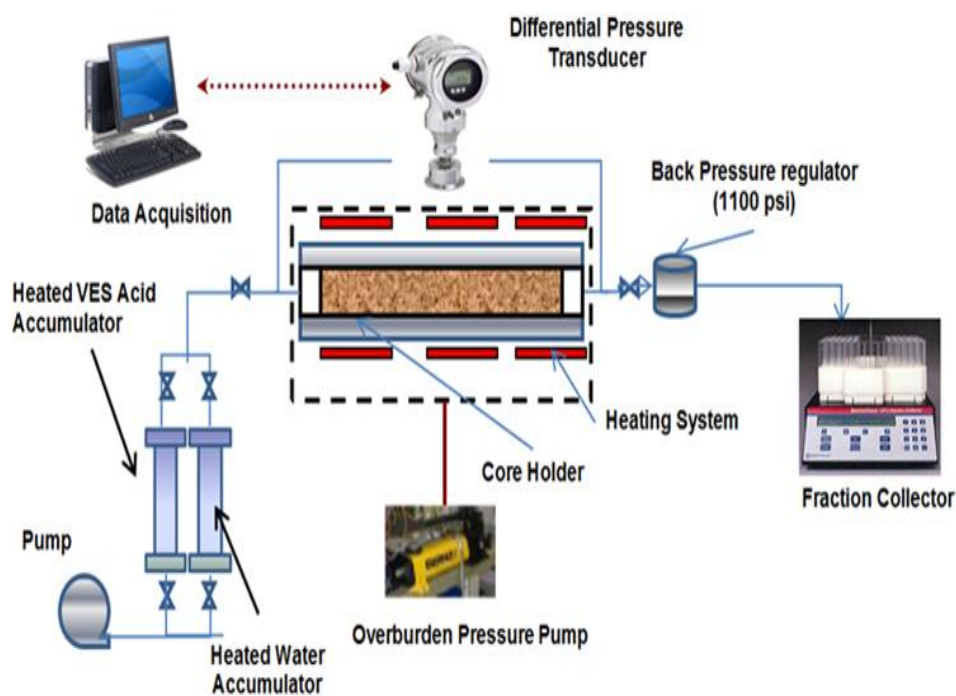


Figure 1. Coreflood Setup

Inductively Coupled Plasma (ICP) Apparatus

Inductively Coupled Plasma (ICP) atomic spectroscopy was used to measure the concentration of cations present in the samples collected from dissolution filtrates, and coreflood effluent vials. Using the concentrations of cations in the ICP samples, experimental results and observations can be better explained and analyzed. This is an analytical technique where the ions in question absorb energy (provided by a plasma torch) and thus are promoted from the stable, ground state to an excited, high-energy state. The ions then decay back to the ground state, and release energy of a specific wavelength. Every element possesses its own specific set of energy levels, and subsequently its own set of absorption and emission wavelengths.

The ICP equipment employed in this experimental study was an Optima 2011 Series DV instrument manufactured by Perkin Elmers. This device employed an optical emission spectrometry (OES) technique for the detection of the amount of cations present in solutions. In this technique, the sample was subjected to high temperatures that caused a high amount of collisional excitation in the calcium ions. The ions then decayed to ground state through thermal and radiative energy transitions. The intensity of the light emitted at specific wavelengths was measured and used to determine the concentrations of calcium ions in solution.

Figure 2 illustrates the ICP apparatus:

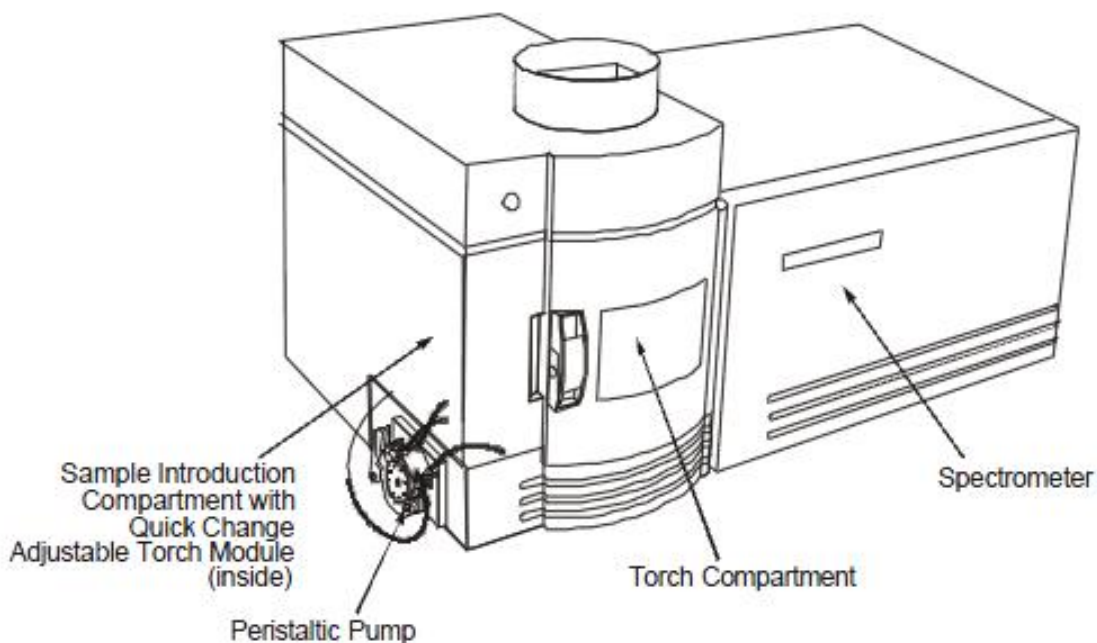


Figure 2. ICP Apparatus

Scanning Electron Microscope (SEM-EDS) Apparatus

Scanning electron microscopy (SEM) is a type of microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with electrons in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. SEM can achieve resolution better than a nanometer. Figure 3 shows the Evex Mini SEM Unit used in this study.



Figure 3. Evex Mini SEM Unit

In this study SEM is used to analyze precipitate in clay dissolution residue samples. To use the equipment, the samples need to be prepared carefully first. The samples were prepared by crushing them into fine particles. Then the crushed samples

were mounted on a double stick carbon tape and coated with a thin film of gold. To coat the samples with gold, MSC-1000 Mini sputter coater was utilized. Figure 4 shows the specific sputter coater used for the experiments.



Figure 4. MSC-1000 Mini Sputter Coater

The coated samples were then inserted into the SEM mounting chamber and examined at. Figure 5 illustrates the chamber next to the camera where samples were inserted. A proprietary SX-3000 was the software used to provide the image and EvexNanoAnalysis was used to run the elemental analysis portion of the experiment.



Figure 5. SEM Mounting Chamber

Sieve Tray Apparatus

A sieve is an open container, usually cylindrical, that has a mesh or a screen at the bottom. The mesh is uniform, with a high degree of precision in the spacing and the size of the openings. Sieve analysis involves selecting and organizing individual sieves that permits the majority of a sample's grains to be collected within the suite and provides a large enough distribution for analysis. Typically, the sieves are referred to by their sieve number, which has been established by a standards committee that developed the sieve system.

The clean sieves are weighed individually and stacked with the coarsest screen on top. A pan at the base of the stack collects the fine clays. The bottom of the assembly is solid and has latex sides.

Once the sieve suite has been selected, the sample is placed in the top sieve. The sample is sifted through successive screens. The sonic sifter provides a vertical, oscillating column of air and a repetitive mechanical pulse to move the grains through the system. In contrast to a mechanical sifter, a sonic sifter produces little abrasion and thus reduces wear and tear. As the grains pass from the top sieve downward, the larger particles are retained in the sieves with mesh smaller than the diameter of the grains. When the process is completed, the individual sieves and their contents are weighed.

Sandstone Core Samples

Berea and Bandera core samples of 6 inch length and 1.5 inch diameter were used. These cores were cut from huge blocks provided to our research group. Each core was dried, weighed and saturated to find out its porosity prior to coreflood experiments.

Clay Samples

Kaolinite, Illite, Chlorite and Bentonite samples were all used for dissolution experiments using citric acid and mud acid. Each clay was carefully dried, weighed and run through the sieve tray apparatus to ensure uniform grain size for experiments.

Citric Acid

Powder purchased with a purity of 99.5%, and used as is.

HydroChloric Acid (HCl)

Purchased originally at a purity of 36.5%, diluted for experiments as required. pKa value of -9.

Hydrofluoric Acid (HF)

Prepared at desired concentrations using HCl and AmmoniumBiFluoride (ABF).
pKa value of 3.14.

DeIonized (DI) Water

Collected from DI water stations in labs for acid preparation. DI water is free of any free ions and causes fewer problems in acid preparation.

Ammonium Chloride

Used as for brine preparation during coreflood experiments and also to saturate the sandstone cores prior to acid injection.

Na-GLDA

L-glutamic acid N,N-diacetic acid (pKa = 3.5) was obtained from Akzo Nobel at 47% purity. It was diluted for experiments as required.

Corrosion Inhibitor (CI) and Corrosion Inhibitor Intensifier (CII)

Proprietary additives supplied by Schlumberger. Used in specific concentrations as outlined by the MSDS.

Methods

Acid Preparation

Most chemicals including Na-GLDA, Hydrochloric acid (HCl), Ammonium Chloride were prepared to the desired concentration by diluting with DI water. HF was prepared using Ammonium BiFluoride (ABF), HCl and DI water. To begin with, HCl and DI water were weighed and added to a beaker with a magnetic stirrer. The appropriate amount of ABF was then added to the beaker, and the mixture was stirred for about 30 minutes.

Mud acid used for citric acid clay dissolution experiments was prepared at a 9:1 weight ratio of HCl to HF. HF was first prepared at the required concentration, and HCl was added to obtain a 9:1 mixture. Citric acid was added directly to the mud acid mixture prior to dissolution experiments as needed. Acid mixtures for the coreflood experiments were prepared by carefully adding 20 wt% Na-GLDA to 1 wt% HF, to ensure no incompatibilities and precipitate formation.

Clay Dissolution Experiments

For clay dissolution experiments, each clay was first dried to remove moisture, and then weighed. Clay samples were run through the sieve analysis apparatus to obtain

uniform clay particles. For each set of dissolution experiments, 20 grams of clay were reacted with 2 grams of acid in a beaker with a magnetic stir bar for 30 minutes. Upon completing the reaction, the residue and filtrate were separated using filter paper. The filtrate was collected in a 50ml vial, and diluted as required before ICP analysis. The filtrate was carefully washed multiple times to remove any fluorine before being dried and was subsequently analyzed using SEM-EDS.

The filtrate obtained was diluted to a factor of 1000 and analyzed using ICP for concentrations of cations in the samples. The residue was analyzed for precipitates using SEM-EDS. The results from the analytical methods was very helpful in determining the suitability of using the desired acid with clays.

Compatibility Studies between Na-GLDA and HF at Varying Concentrations

Before running coreflood experiments using Na-GLDA and HF, it was necessary to run compatibility tests between the two chemicals at different concentrations. This was done to test whether any problems or precipitates arose when using this mixture. Another reason this was done was to find an optimum acid mixture formulation that maximizes dissolution capabilities and minimizes formation damage due to precipitates.

For each compatibility tests, the necessary amounts of Na-GLDA and HF were weighed using a balance and mixed together in a beaker using a magnetic stir bar. The mixture was mixed continuously for 30 minutes, after which the beaker was inspected for any precipitate or incompatibilities. The contents of the beaker were emptied into a

sample vial using filter paper to ensure no residue enters the filtrate. The residue, if found, was dried and washed using DI water to remove any fluorine from the residue. The dried residue was analyzed using SEM-EDS and the results were reported.

Core Preparation and Coreflood Experiments

Prior to all coreflood experiments, core samples were first dried at 150°F for 4 hours, weighed immediately after and saturated in 5 wt% NH₄Cl for a day. After saturation was complete, the core was weighed again, and the porosity was calculated using the initial and final weights of the core. Once the porosity for a core was calculated, initial permeability experiments were conducted on the core using the coreflood apparatus. Instead of injecting an acid, 5 wt% NH₄Cl brine was injected into the core at varying flowrates and using LabView®, a pressure drop versus time graph was generated to estimate the initial permeability of the core in millidarcy.

The permeability was determined using Darcy's Law, which is a frequently used mathematical equation for fluid flow in porous media. It represents the volumetric flow rate as a function of the area, elevation or distance, fluid pressure and a proportionality constant known as k, the permeability constant. The equation can be applied to numerous cases depending on flow criteria. For the case of coreflood experiments in the lab, a one dimensional steady state flow regime is used to calculate the permeability. The equation for this case is given by the following formula:

$$\left(\frac{Q}{A}\right) = \left(\frac{k}{\mu}\right) * \left(\frac{\Delta P}{L}\right)$$

where,

Q = Volumetric Flowrate (m^3/s)

A = Cross Sectional Area (m^2)

k = Permeability (darcy)

μ = viscosity (cP)

ΔP = Pressure Drop (Psi)

L = Length of Core (m)

Once the initial permeability was estimated, the next step was to prepare the main acid, preflush and postflush using the guidelines outlined for the experiment. Before injecting any chemicals, a metal sleeve was wrapped around the core holder, and the controller was set to the desired temperature of 300 °F. Once the desired temperature was reached, 5 wt% NH_4Cl brine was injected till the pressure drop stabilized, after which 20 wt% Na-GLDA was injected as a pre-flush as well. Once the required pore volume or PV of the preflush was used, the main acid was injected into the core. After the necessary PV of main acid was injected a post-flush was run using ammonium chloride brine. During the course of each injected, from pre-slush to post-flush, effluent samples were collected every 6 minutes. These were later diluted to a factor of 1000 and analyzed using ICP for cation concentrations as the experiment proceeded.

Once the post-flush stage has been completed, 5 wt% NH_4Cl was injected into the core again to calculate the final permeability. The flow rate was varied according to the initial permeability experiments and the pressure versus flow rate data was used to

estimate a final permeability. At the end of the coreflood experiment, each chemical accumulator was cleaned thoroughly and DI water was run through the entire coreflood setup to remove any remaining acid and particulates.

CHAPTER III

INVESTIGATE THE USE OF CITRIC ACID WITH 9:1 MUD ACID FOR CLAY DISSOLUTION PURPOSES

Experimental Outline

The purpose of this experiment was to evaluate the use of citric acid along with 9:1 mud acid for clay dissolution purposes, and compare its performance against regular 9:1 mud acid. First, all four clay types: kaolinite, illite, chlorite, and bentonite were reacted with just 9:1 mud acid. This was followed by dissolution experiments using 9:1 mud acid along with different concentrations of citric acid added to it. Table 1 summarizes the chemical formulations used for each dissolution experiment.

Table 1. Citric Acid Dissolution Formulation Table

Experiment #	Chemical Composition
1	9:1 Mud Acid
2	9:1 Mud Acid + 1 wt% Citric Acid
3	9:1 Mud Acid + 3 wt% Citric Acid
4	9:1 Mud Acid + 5 wt% Citric Acid

As outlined in the methods section, 20 grams of clay was treated with 2 grams of the acid for 30 minutes at room temperature. The filtrate and residue were separated,

collected, and prepared for analysis. The results from both ICP and SEM-EDS analysis were tabulated for further investigation and comparison.

Experiment # 1: 9:1 Mud Acid Only

1. Kaolinite

The ICP and SEM results are presented in Table 2 and Table 3 respectively.

Table 2. ICP Results Kaolinite Experiment # 1

Ion	Silicon	Aluminum
Conc. (ppm)	3142	2769

Table 3. SEM Results Kaolinite Experiment # 1

Element	Wt%
O	50.16
Al	15.86
Si	19.3
Cl	14.68

2. Chlorite

The ICP and SEM results are presented in Table 4 and Table 5 respectively.

Table 4. ICP Results Chlorite Experiment # 1

Ion	Silicon	Aluminum	Iron	Magnesium
Conc. (ppm)	2683	1958	1907	2192

Table 5. SEM Results Chlorite Experiment # 1

Element	Wt%
O	43.3
MG	14.77
Al	13.35
Si	13.95
Cl	2.79
Fe	11.65

3. Illite

The ICP and SEM results are presented in Table 6 and Table 7 respectively.

Table 6. ICP Results Illite Experiment # 1

Ion	Silicon	Aluminum	Iron	Magnesium
Conc. (ppm)	2908	1416	1681	622

Table 7. SEM Results Illite Experiment # 1

Element	Wt%
Mg	1.65
Si	25.04
Al	11.38
Fe	3.93

4. Bentonite

The ICP and SEM results are presented in Table 8 and Table 9 respectively.

Table 8. ICP Results Bentonite Experiment # 1

Ion	Silicon	Aluminum	Iron
Conc. (ppm)	3429	1150	0

Table 9. SEM Results Bentonite Experiment # 1

Element	Wt%
Mg	1.91
Si	10.89
Al	29.7
O	43.88

Experiment # 2: 9:1 Mud Acid + 1 wt% Citric Acid

1. Kaolinite

The ICP and SEM results are presented in Table 10 and Table 11 respectively.

Table 10. ICP Results Kaolinite Experiment # 2

Ion	Silicon	Aluminum
Conc. (ppm)	3700	3325

Table 11. SEM Results Kaolinite Experiment # 2

Element	Wt%
O	46.56
Si	17.77
Al	18.59
Au	17.08

2. Chlorite

The ICP and SEM results are presented in Table 12 and Table 13 respectively.

Table 12. ICP Results Chlorite Experiment # 2

Ion	Silicon	Aluminum	Iron	Magnesium
Conc. (ppm)	2438	1877	1600	1929

Table 13. SEM Results Chlorite Experiment # 2

Element	Wt%
O	38.03
Mg	16.97
Al	15.06
Si	15.48
Fe	14.46

3. Illite

The ICP and SEM results are presented in Table 14 and Table 15 respectively.

Table 14. ICP Results Illite Experiment # 2

Ion	Silicon	Aluminum	Iron	Magnesium
Conc. (ppm)	3062	1566	1764	725

Table 15. SEM Results Illite Experiment # 2

Element	Wt%
Fe	3.2
Al	12.44
Si	33.88
Mg	1.64

4. Bentonite

The ICP and SEM results are presented in Table 16 and Table 17 respectively.

Table 16. ICP Results Bentonite Experiment # 2

Ion	Silicon	Aluminum
Conc. (ppm)	3429	1150

Table 17. SEM Results Bentonite Experiment # 2

Element	Wt%
O	31.97
Al	7.26
Si	13.38
Au	17.6
Au	29.79

Experiment # 3: 9:1 Mud Acid + 3 wt% Citric Acid

1. Kaolinite

The ICP and SEM results are presented in Table 18 and Table 19 respectively.

Table 18. ICP Results Kaolinite Experiment # 3

Ion	Silicon	Aluminum
Conc. (ppm)	2291	2357

Table 19. SEM Results Kaolinite Experiment # 3

Element	Wt%
O	46.56
Si	17.77
Al	18.59
Au	17.08

2. Chlorite

The ICP and SEM results are presented in Table 20 and Table 21 respectively.

Table 20. ICP Results Chlorite Experiment # 3

Ion	Silicon	Aluminum	Iron	Magnesium
Conc. (ppm)	1915	1434	1470	1608

Table 21. SEM Results Chlorite Experiment # 3

Element	Wt%
Mg	14.43
Al	17.85
Si	18.39
Fe	12.82

3. Illite

The ICP and SEM results are presented in Table 22 and Table 23 respectively.

Table 22. ICP Results Illite Experiment # 3

Ion	Silicon	Aluminum	Iron	Magnesium
Conc. (ppm)	2173	1063	1346	558

Table 23. SEM Results Illite Experiment # 3

Element	Wt%
Mg	2.18
Al	14.87
Si	40.66
Fe	0.96

4. Bentonite

The ICP and SEM results are presented in Table 24 and Table 25 respectively.

Table 24. ICP Results Bentonite Experiment # 3

Ion	Silicon	Aluminum
Conc. (ppm)	2964	1013

Table 25. SEM Results Bentonite Experiment # 3

Element	Wt%
Al	13.92
Si	29.62
Au	56.46

Experiment # 4: 9:1 Mud Acid + 5 wt% Citric Acid

1. Kaolinite

The ICP and SEM results are presented in Table 26 and Table 27 respectively.

Table 26. ICP Results Kaolinite Experiment # 4

Ion	Silicon	Aluminum
Conc. (ppm)	2127	2376

Table 27. SEM Results Kaolinite Experiment # 4

Element	Wt%
Al	21.11
Si	21.4
Au	57.5

2. Chlorite

The ICP and SEM results are presented in Table 28 and Table 29 respectively.

Table 28. ICP Results Chlorite Experiment # 4

Ion	Silicon	Aluminum	Iron	Magnesium
Conc. (ppm)	1911	1447	1452	1581

Table 29. SEM Results Chlorite Experiment # 4

Element	Wt%
Mg	19.25
Al	17.47
Si	18.51
Fe	15.97

3. Illite

The ICP and SEM results are presented in Table 30 and Table 31 respectively.

Table 30. ICP Results Illite Experiment # 4

Ion	Silicon	Aluminum	Iron	Magnesium
Conc. (ppm)	2020	1028	1285	484

Table 31. SEM Results Illite Experiment # 4

Element	Wt%
Mg	2.35
Al	17.72
Si	61.77
Fe	5.66

4. Bentonite

The ICP and SEM results are presented in Table 32 and Table 33 respectively.

Table 32. ICP Results Bentonite Experiment # 4

Ion	Silicon	Aluminum
Conc. (ppm)	3057	1036

Table 33. SEM Results Bentonite Experiment # 4

Element	Wt%
Mg	2.36
Al	16.16
Si	44.7
K	1.04
Fe	5.45

Results

The discussion section for this experiment is divided according to each clay type. It makes it easier to understand the results and provides an explanation to acid performance with each clay specifically.

Kaolinite

Kaolinite has a stacked structure with a tetrahedral sheet of silicon linked to an alumina octahedral sheet of oxygen as seen in Figure 6. The clay mineral has equal concentration of aluminum and silicon in its structure, hence the dissolution is expected to be in stoichiometric proportions.

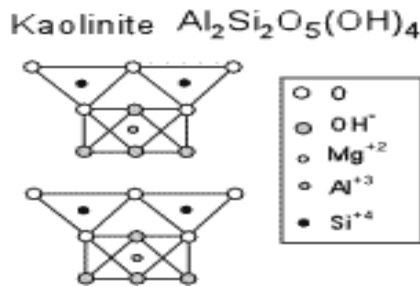


Figure 6. Kaolinite Structure

The ICP and SEM results for kaolinite using all for acids shows that 9:1 mud acid + 1 wt% citric acid performed the best. It was able to extract the maximum amount of silicon and aluminum, whilst keeping the precipitate concentrations low. Increasing the concentration of citric acid caused a reduction in dissolution, and the precipitation increased as well (except when adding 3 wt% citric acid to 9:1 mud acid).

Chlorite

Chlorites have a three layer stacked structure with two tetrahedral layers of silica with an octahedral layer of iron or aluminum in between as illustrated in Figure 7. In chlorites, there are magnesium atoms present in the structure too. The clay mineral has almost two atoms of silicon for every atom of aluminum. This clay has iron present in it, and controlling the iron precipitates is one of most important factors in dealing with chlorite.

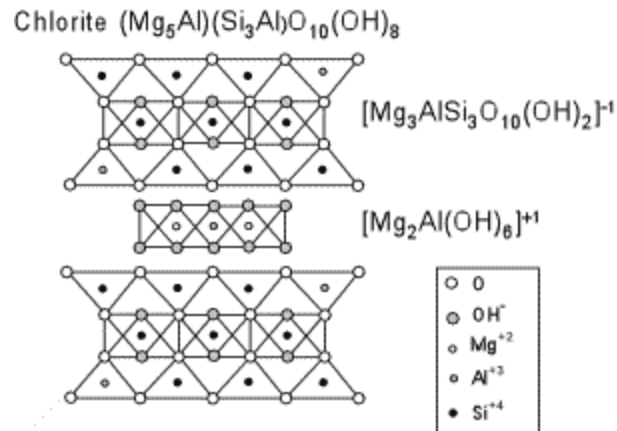


Figure 7. Chlorite Structure

The ICP and SEM results for chlorite suggests that regular 9:1 mud acid was the most effective acid formulation. It extracted the most ions from the clay and caused the least precipitate problems. 9:1 mud acid + 5 wt% citric acid caused the most precipitation and extracted the least amount of cations. This result is similar to that seen with kaolinite, where increasing the concentration of citric acid to 5 wt% causes more problems.

Illite

Illite has a three layer structure as shown in Figure 8, in which an aluminum sheet sandwiched between two silica sheets. The ratio of silicon atoms to aluminum atoms is 2:1. Illite contains potassium between the layers making it a non-swelling clay. Illite has been known to be HCl sensitive, and can cause migration of small needle like fines that block pore throats.

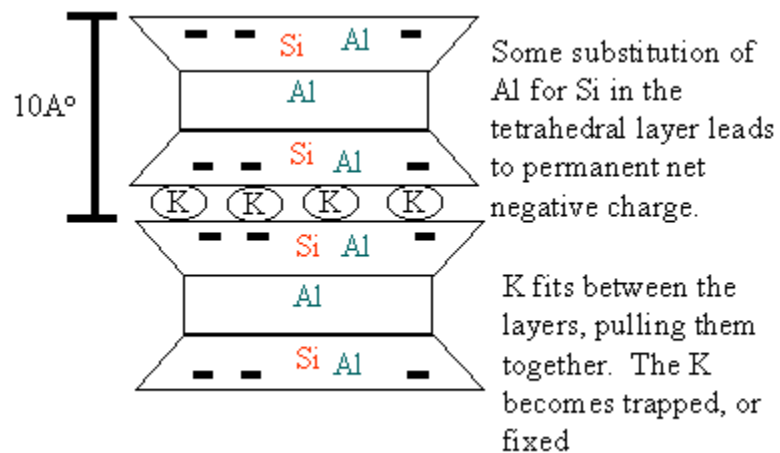


Figure 8. Illite Structure

Analyzing the ICP and SEM data for illite, it is clear that 9:1 mud acid + 1 wt% citric acid provides the best performance, both in terms of cation leaching power and precipitate formation. 9:1 mud acid + 5 wt% citric acid had the worst results, it leached the least amount of cations and caused the most precipitation.

Bentonite

Bentonite, also known as smectite or montmorillonite, consists of three layers, where a central octahedral alumina structure is sandwiched between two tetrahedral silica layers. Between the reticular structure, cation exchange happens regularly, leading to migration of ions to the outside of the lattice, this is the reason bentonite is also referred to as a swelling clay. Figure 9 illustrates the structure of bentonite.

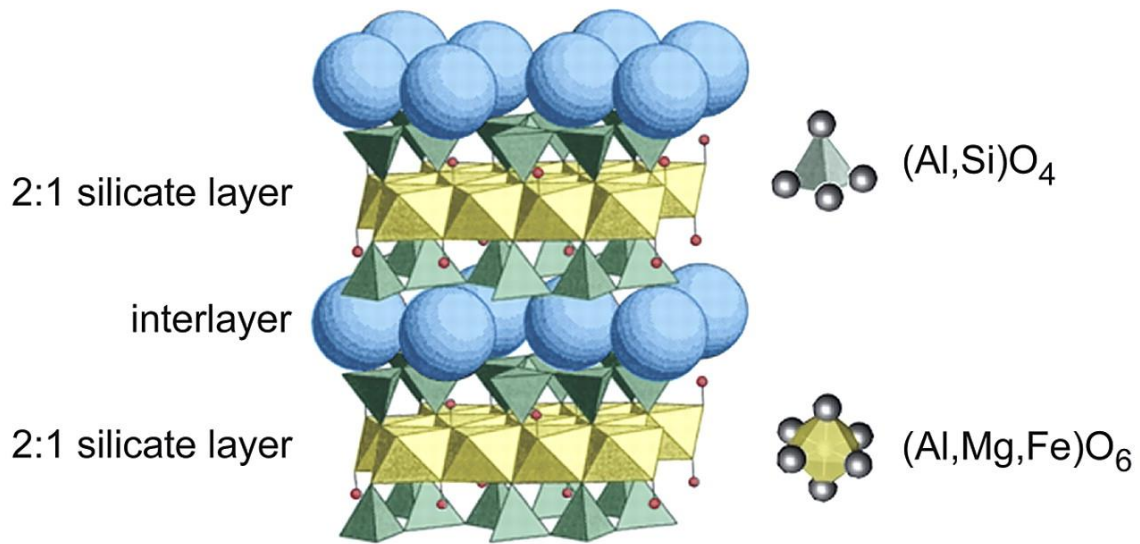


Figure 9. Bentonite Structure

The ICP and SEM results are a little varied for bentonite, in terms of ion leaching, 9:1 mud acid + 1 wt% citric acid performs the best, while 9:1 mud acid + 3wt% citric acid leached the least amount of cations from the clay. In terms of precipitate formed, 9:1 mud acid + 5wt% had the worst results, causing the maximum amount of precipitate formation.

Discussion

The results for all clays clearly show that increasing the concentration of citric acid to 9:1 mud acid, reduces the performance of the acid mixture. It has been previously studied (Al-Khaldi et. al 2003) that pH, temperature and ionic strength are three factors that determine if reaction products of citric acid will form water insoluble or water

soluble compounds with magnesium, calcium and iron. According to the research, complexes formed by citric acid precipitate at lower temperatures, higher organic acid concentration and at low pH as well. This explains the results with respect to magnesium and iron precipitates because the experiments were conducted at room temperature, and as the concentration of citric acid was increased the precipitation of certain precipitates increased as well. The low pH in the acid mixture also could have prevented magnesium complexes to form, and thus resulted in precipitation.

The precipitation of aluminum and silicon salts has not been experimentally studied and validated a lot. Karbouj (2007) showed that aluminum chelation with citric acid is dependent on temperature and at low temperatures this chelation is not very strong. This could explain why aluminosilicate precipitation was observed in all experiments. The increasing precipitation with increasing concentrations of citric acid could be credited to the low temperature, higher acid concentration and low pH.

CHAPTER IV

INVESTIGATE THE USE OF SODIUM GLDA FOR SANDSTONE ACIDIZING PURPOSES

Experimental Outline

The goals of this experiment were to study the compatibility of Na-GLDA along with HF, and to evaluate its performance for sandstone acidizing purposes. This experiment was divided into two parts:

1. Compatibility study between Na-GLDA and HF to estimate the optimum acid mixture formulation that can be used for coreflood experiments without any incompatibilities. Any incompatibilities found were then analyzed using the SEM-EDS apparatus.
2. Coreflood analysis using the optimum acid mixture formulation on Berea and Bandera cores at 300°F.

Compatibility Studies

Before coreflood experiments can be run using new chemical mixtures, a compatibility study must be done. This ensures that there are no problems encountered during coreflood experiments due to incompatibilities such as precipitate formation, and it also helps identify the optimum mixture formulation to help maximize results. For this compatibility study four experiments were conducted using different concentrations of both Na-GLDA and HF. Each experiment was performed under the guidelines and

methods outlined in the methods section. The required chemicals were diluted to the desired concentrations as needed. Once the experiments were completed the beakers were visually inspected for any precipitate formation, and reported accordingly.

Presented next are the set of different Na-GLDA and HF concentrations that were tested in each experiment.

Experiment # 1

For this experiment 15 wt%, 20 wt%, and 30 wt% Na-GLDA was tested with 0.5 wt%, 1 wt%, and 2 wt% HF to see if any incompatibilities can be found. The results are presented in Table 34 below.

Table 34. Compatibility Study Experiment # 1

Na-GLDA (wt%)	HF (wt%)	Precipitation (Y/N)
15	0.5	N
15	1	N
15	2	Y
20	0.5	N
20	1	N
20	2	Y
30	0.5	Y
30	1	Y
30	2	Y

The results from this experiment proved to be very useful because it is clear that if the Na-GLDA concentration exceeds 20 wt% and HF concentration exceeds 1 wt% there will be a precipitate formed. Therefore, there must be a critical sodium to fluorine ratio that determines when the precipitate formed. Figure 10 shows the precipitation observed.



Figure 10. Precipitation Seen in 20 wt% Na-GLDA + 2 wt% HF

Experiment # 2

For this experiment the HF concentration was kept fixed at 1 wt% HF, and the Na-GLDA concentration was varied.

Table 35. Compatibility Study Experiment # 2

Na-GLDA (wt%)	HF (wt%)	Precipitation (Y/N)
3	1	N
5	1	N
10	1	N
13	1	N
15	1	N
20	1	N

As seen in Table 35 above, none of the samples had any precipitate formation suggesting that if the concentration of HF is kept at 1 wt% or below there shouldn't be any incompatibilities, and these results also show that if the Na-GLDA concentration is kept below 20 wt% there shouldn't be any precipitation as well.

Experiment # 3

For this experiment, the effect of sodium concentration was evaluated. This was done by adding 3 wt% NaCl salt to the acid mixture to see if there is a critical sodium concentration above which precipitation occurred. One again the Na-GLDA concentration was varied and the HF concentration was kept fixed at 1 wt%.

Table 36. Compatibility Study Experiment # 3

Na-GLDA (wt%)	HF (wt%)	NaCl (wt%)	Precipitation (Y/N)
1	1	3	N
5	1	3	N
10	1	3	N
15	1	3	N
20	1	3	Y
25	1	3	Y

From Table 36 above, it can be inferred that adding any form of sodium to an existing acid mixture with Na-GLDA concentration exceeding 20 wt% whilst keeping the HF concentration at 1 wt% will cause incompatibilities. This gave us vital information on the compatibility between Na-GLDA and HF, and helped identify an optimum acid mixture formulation.

Experiment # 4

This experiment was conducted to re-affirm the previous experiments results and finalize an optimum acid mixture formulation. By maximizing the concentration of the acid mixture formulation, the amount of cation leaching/dissolution as well as cation chelation can be maximized. 15 wt% and 20 wt% Na-GLDA were tested with 1 wt% HF and 1 wt% NaCl.

Table 37. Compatibility Study Experiment # 4

Na-GLDA (wt%)	HF (wt%)	NaCl (wt%)	Precipitation (Y/N)
15	1	1	N
20	1	1	Y

As seen in Table 37 above, the last experiment confirmed our previous results. The optimum acid mixture formulation that can be used without any incompatibilities prior to injection is achieved when 20 wt% Na-GLDA is mixed with 1 wt% HF.

Precipitate Analysis

Before proceeding with coreflood experiments it was decided that the precipitate found in the compatibility studies should be analyzed and possibly identified. In order to do this, as outlined in the methods section earlier, the precipitate residue was washed, dried and analyzed using SEM-EDS equipment.

Figure 11 shows the SEM image of the precipitate residue found from the incompatibility between Na-GLDA and HF.

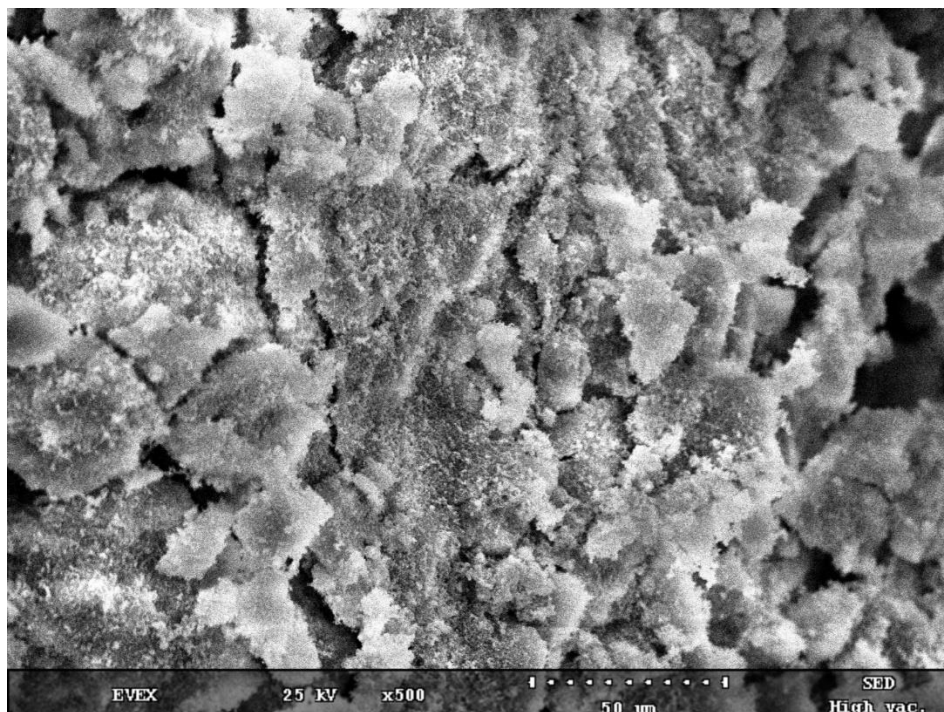


Figure 11. SEM image of Fluoride Salt of Sodium

Following the SEM, an elemental analysis was completed using the SEM-EDS apparatus and the proprietary software included. Figure 12 shows the EDS spectrum for the precipitate.

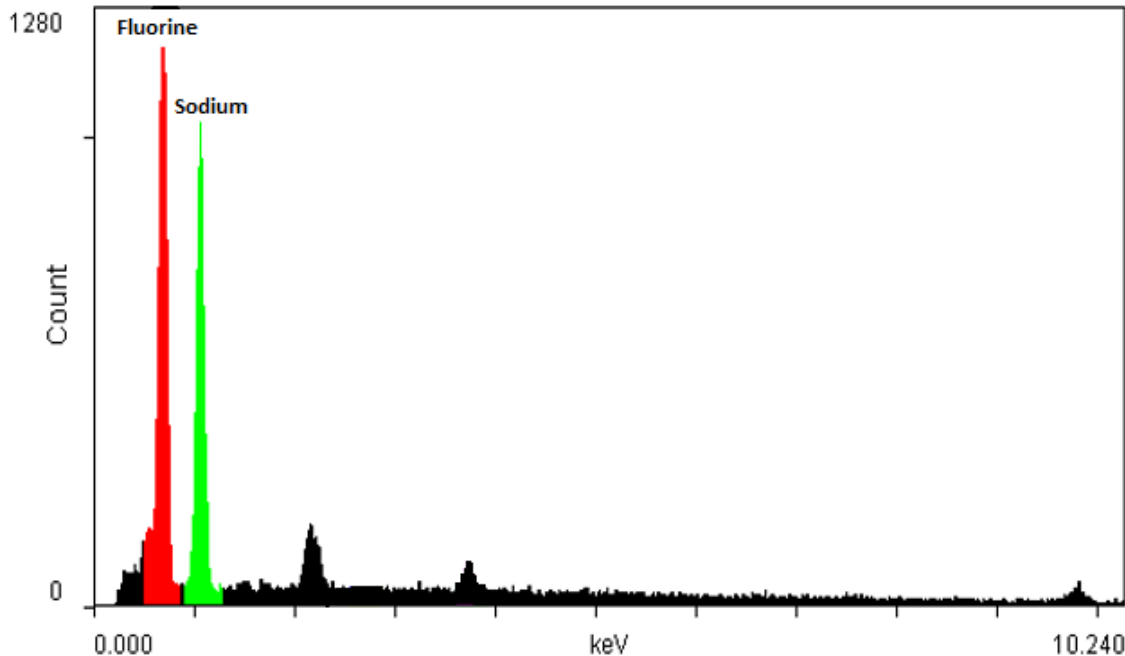


Figure 12. SEM-EDS Spectra Precipitate Run # 1

From the elemental distribution spectra the precipitate was determined to be a fluoride salt of sodium, with a sodium to fluorine molar ratio of about 0.85. This salt precipitate was therefore sodium fluoride or NaF, a common reaction product when sodium ions are reacted with fluorine compounds. After a brief literature survey, it was found that sodium fluoride has high solubility in HF and water; therefore it could not have precipitated out. Further research revealed that sodium fluoride reacts with HF to form NaHF₂ or sodium bifluoride. This salt has very low solubility, about 3g/ml at room temperature, and it explains the precipitate seen during SEM-EDS analysis. Research has shown that sodium bifluoride decomposes with heat and in the presence of water to form NaF and HF (Hudleston and Jehu 1938), this explains why our initial results suggested

the precipitate was sodium fluoride. This because the residue collected was washed with DI water and dried in the oven, causing the NaHF_2 to decompose into NaF . Figure 13 shows the EDS spectrum for the precipitate during the second run.

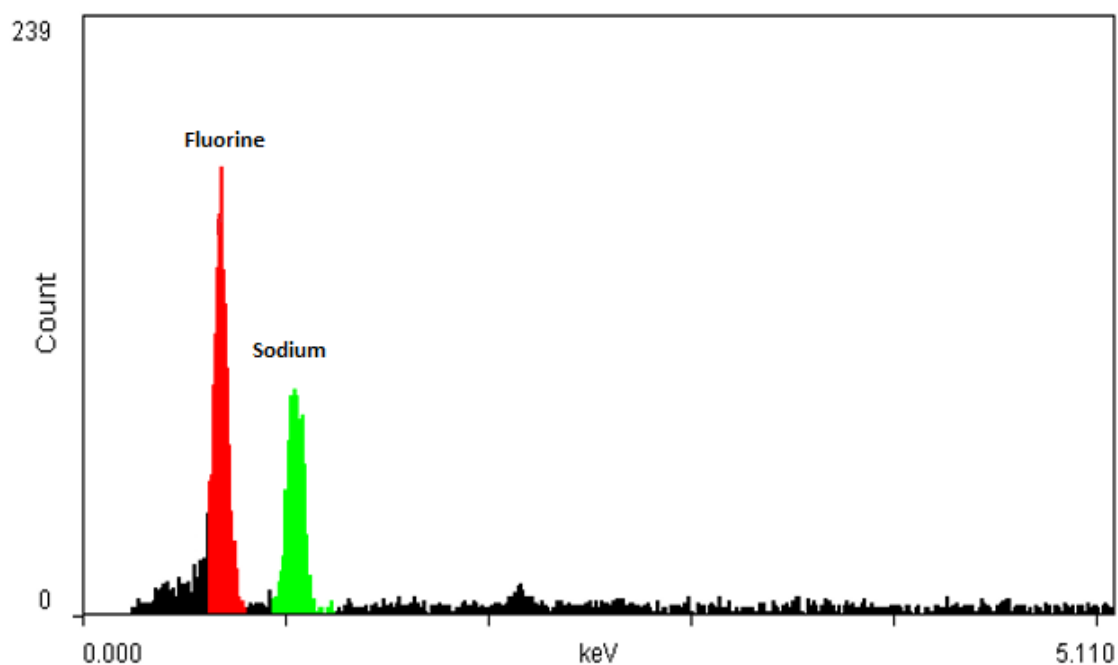


Figure 13. SEM-EDS Spectra Precipitate Run # 2

Coreflood Analysis

The coreflood experiments begin by estimating the porosity and initial permeability of the core using the steps outlined in the methods section. The steps were repeated for both Berea and Bandera cores. Presented below in Table 38, are the porosity and initial permeability results for both cores:

Table 38. Core Properties

Core Type	Core Length (in)	Core Diameter (in)	Porosity (%)	PV (cm ³)	Initial Permeability (mD)
Berea	6	1.5	20	34	55
Bandera	6	1.5	15	26	5.3

Following the estimation of basic core properties, the preflush, main acid, and postflush are prepared as needed. For these experiments, two different preflushes were used: 5 wt% NH₄Cl and 20 wt% Na-GLDA. The reason two preflushes are being used here is because previously it was studied that Na-GLDA can help prevent the precipitation of calcium fluoride (CaF₂) during the early stages of acid injection (De Wolf and Nasr-El-Din 2011). Calcium fluoride is known to precipitate as soon as it comes into contact with HF, thus by injecting 20 wt% Na-GLDA as preflush, the possibility of that precipitation can be minimized. The main acid prepared was 20 wt% Na-GLDA + 1 wt% HF, which was determined from the compatibility studies done prior to this experiment. The postflush used for these experiments was 5 wt% NH₄Cl.

The next step before running the coreflood experiment was to estimate the coreflood parameters such as flowrate and temperature. Previous experiments (De Wolf and Nasr-El-Din 2011) have shown that using a lower flowrate can help with greater soaking time, and provide more time for the acid to interact with the cores. Therefore it

was decided to use a flowrate of 2 cm³/min for both cores. As for the temperature, it was decided to run the experiments at 300°F because this acid mixture formulation will be used for high temperature applications in the future.

Once the coreflood parameters were set, the exact pore volume (PV) of preflush, main acid flush and postflush were estimated. This was done by conducting a thorough literature survey as well as using a calculated engineering decision. Therefore for these experiments it was decided to use the primary preflush of 5 wt% NH₄Cl till the core pressure drop stabilized, once that was achieved 3 PV of secondary preflush, 20 wt% Na-GLDA was injected. Once the secondary preflush injection was complete, the main acid mixture was injected for 4 PV. This was followed by postflush injection of NH₄Cl till the pressure drop across the core was stabilized. Since this work is very novel and introductory, these estimated PV values could be modified in the future depending on situations such as core type, mineralogy, temperature etc.

Now that all the experimental parameters were defined, the coreflood experiment was run as described earlier in the methods section. An outlet valve was utilized to collect core effluent every 6 minutes, and these samples were later used for ICP analysis to study the leached ions. During the entire course of the coreflood experiment, data acquisition software LabView® was used to record pressure drop values every 5 seconds. This helped generate a pressure drop versus PV graph, which helps us understand and observe how the cores reacted to the different stages of injection during the course of the experiment. Once the postflush injection phase was complete, a final permeability run was conducted on both cores to estimate the final permeability after the

core was stimulated. This helps us identify if there was any change in the permeability, which ultimately tells us if the core stimulation using our acid mixture was successful or not. Once the final permeability experiment was complete, excel was used to construct these pressure drop versus PV graphs for the main coreflood experiment, and they are presented in the next few pages.

The effluent samples collected every 6 minutes were first examined visually for any form of precipitation or incompatibilities. Following this, each sample was carefully diluted to a factor of 1000 using DI water for analysis using the ICP apparatus. Once the ICP analysis was complete, excel was utilized to generate a graph showing the concentration of dissolved ions versus PV of preflush, main acid and postflush injected.

Berea Core

The results for the coreflood main experiment using the Berea core are presented graphically. First, the pressure drop across core versus cumulative injected volume graph is shown in Figure 14, followed by the ICP results in Figure 15 and Figure 16 respectively.

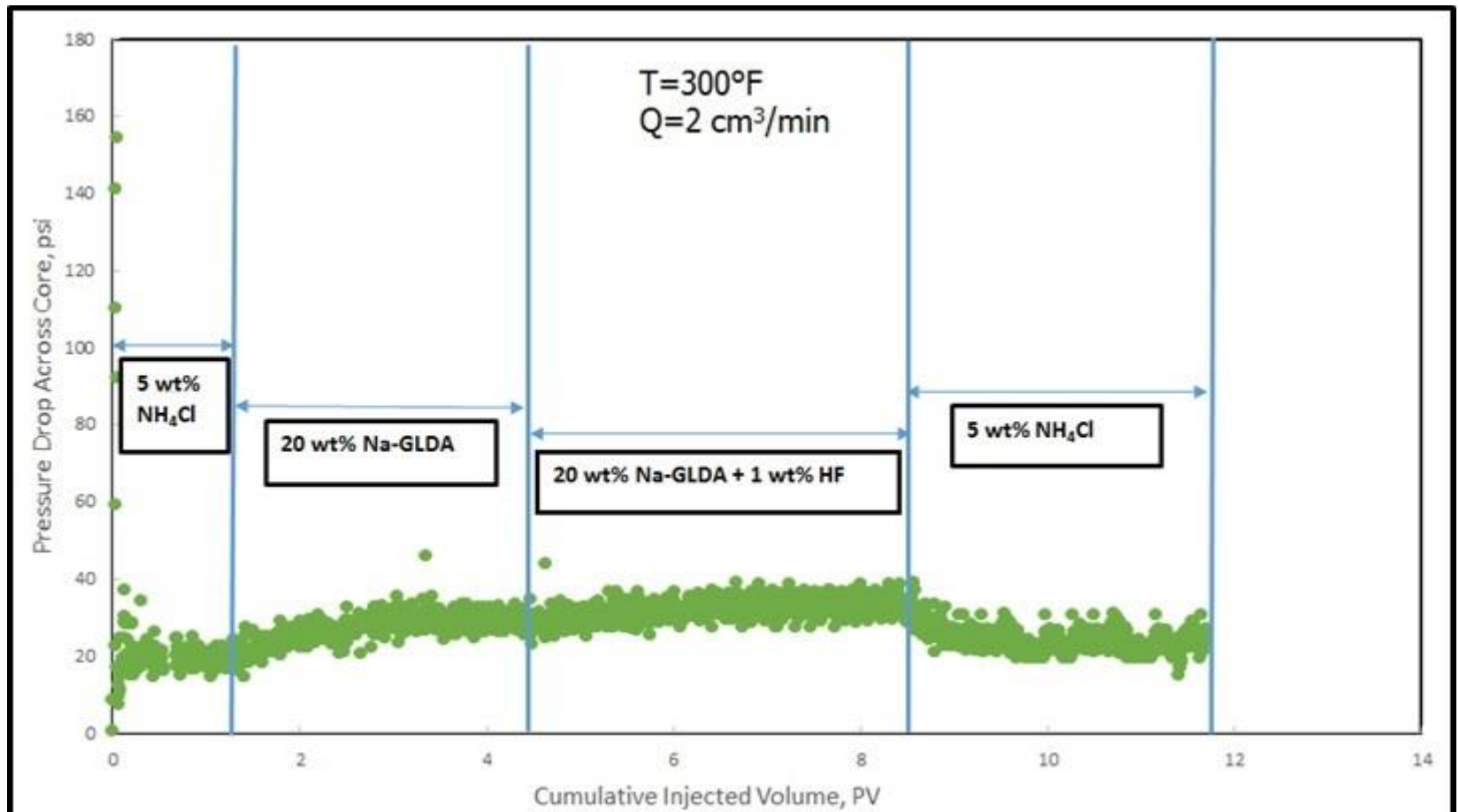


Figure 14. Pressure Drop Graph Berea

As seen in Figure 14, the primary preflush of 5 wt% NH_4Cl was injected till about 1.5 PV, at which point the accumulator for 20 wt% Na-GLDA was activated, pumping the secondary preflush till about 4.5 PV. Following this the main acid mixture of 20 wt% Na-GLDA + 1 wt% HF was injected till approximately 8.5 PV. After this point, the postflush of 5 wt% NH_4Cl was injected till the core pressure drop stabilized. From the graph it is clear that once the secondary preflush is injected the pressure drop increases, this is due to a higher viscosity fluid entering the core. The pressure buildup continues further due to dissolution, and possible blocking of pore throats by precipitation, until a steady state pressure is achieved. The same pressure increase happens when the main acid mixture is injected at about 4.5 PV. At the end of the main acid injection, the pressure drop decreases, suggesting dissolution of ions resulting in the clearing up of pore throats. Postflush injection shows a steady decline in pressure drop due to the injection of a lower viscosity ammonium chloride, and also due to further clearing of pore throats by movement of already dissolved or chelated ions to the outlet of the core holder. Next we analyze the ICP results from the effluent samples.

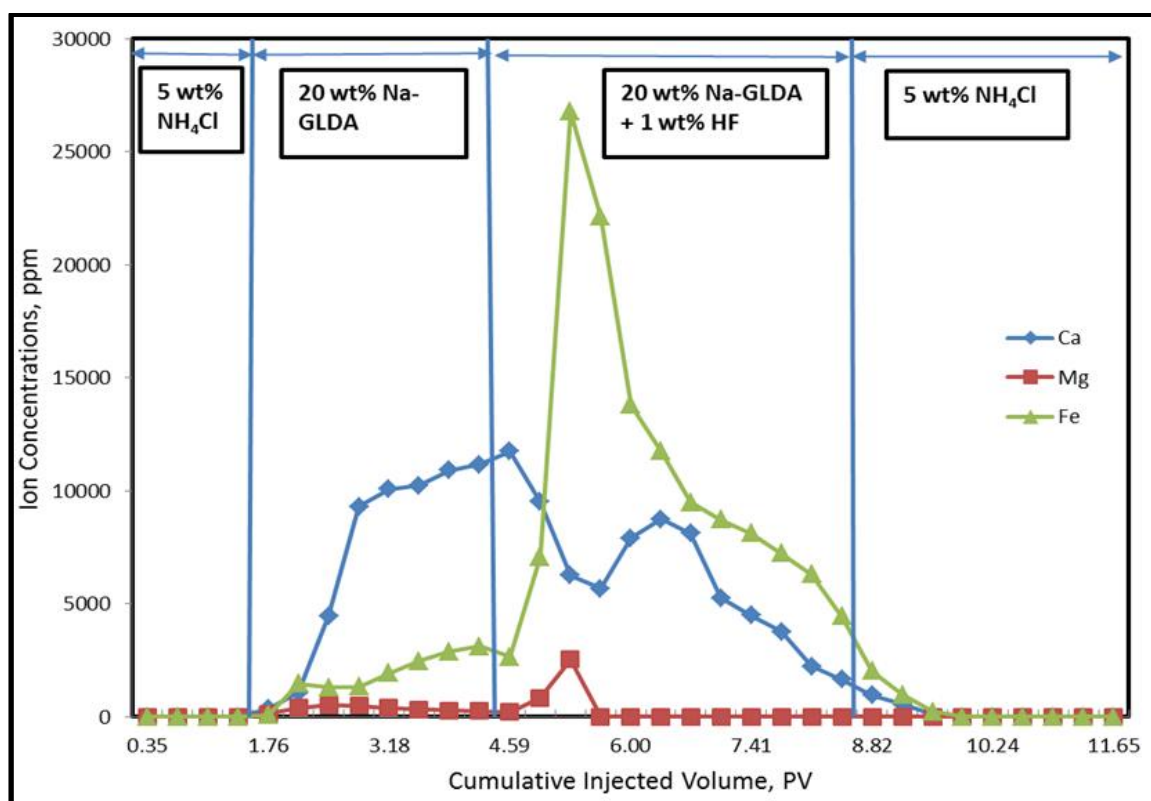


Figure 15. ICP Results Berea

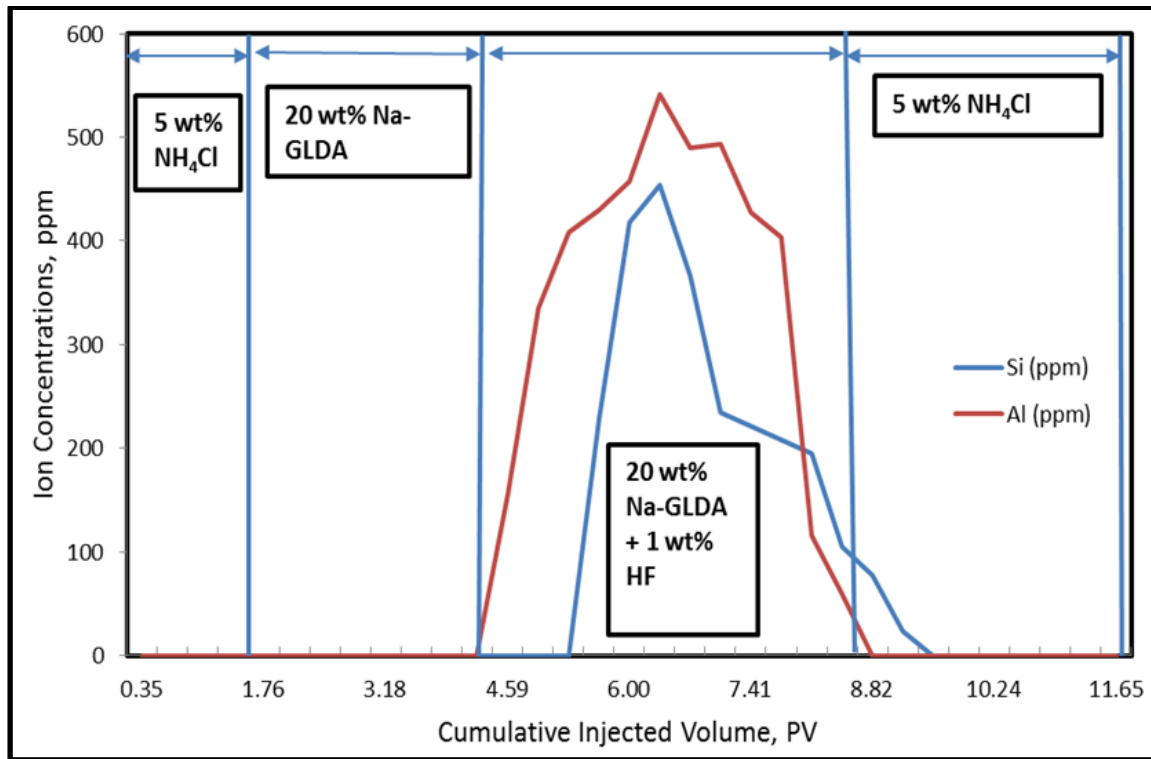


Figure 16. ICP Results Aluminum and Silicon Dissolution Berea

The ICP results clearly indicate that the secondary preflush of 20 wt% Na-GLDA and the main acid mixture of 20 wt% Na-GLDA + 1 wt% HF were successfully able to leach iron, calcium and magnesium ions from the core but were not as successful with aluminosilicates. This was expected because Na-GLDA is a chelating agent and it has an affinity towards divalent and trivalent cations, which in this case was iron, calcium and magnesium. Another point to note is that the secondary preflush of 20 wt% Na-GLDA was able to chelate to a high amount of calcium, making it a very useful option as a preflush when acidizing sandstone cores because it can help reduce the precipitation of CaF_2 . The last and most obvious observation is the poor leaching of aluminum and

silicon, which make up the clays. The primary goal of the main acid mixture is to dissolve these cations, but as seen in the graph above very low concentrations of both were leached from the core. This could mean two things:

1. The main acid mixture did successfully dissolve aluminum and silicon, but changes in pH and preferential chelation of iron, calcium and magnesium over the aluminosilicates (by Na-GLDA) caused them to precipitate within the core. This also explains the increased pressure drop during the secondary preflush and main acid injection phases.
2. The injection of secondary preflush somehow hindered the interaction between HF and the aluminosilicates. This could be because Na-GLDA possibly coated the core surface prior to the main acid injection phase preventing any contact between HF and aluminosilicates.

Bandera Core

The results for the coreflood experiment using the Bandera core are presented next. Similar to the Berea results, the pressure drop across core versus cumulative injected volume graph is shown first in Figure 17, followed by the ICP results in Figure 18 and Figure 19 respectively.

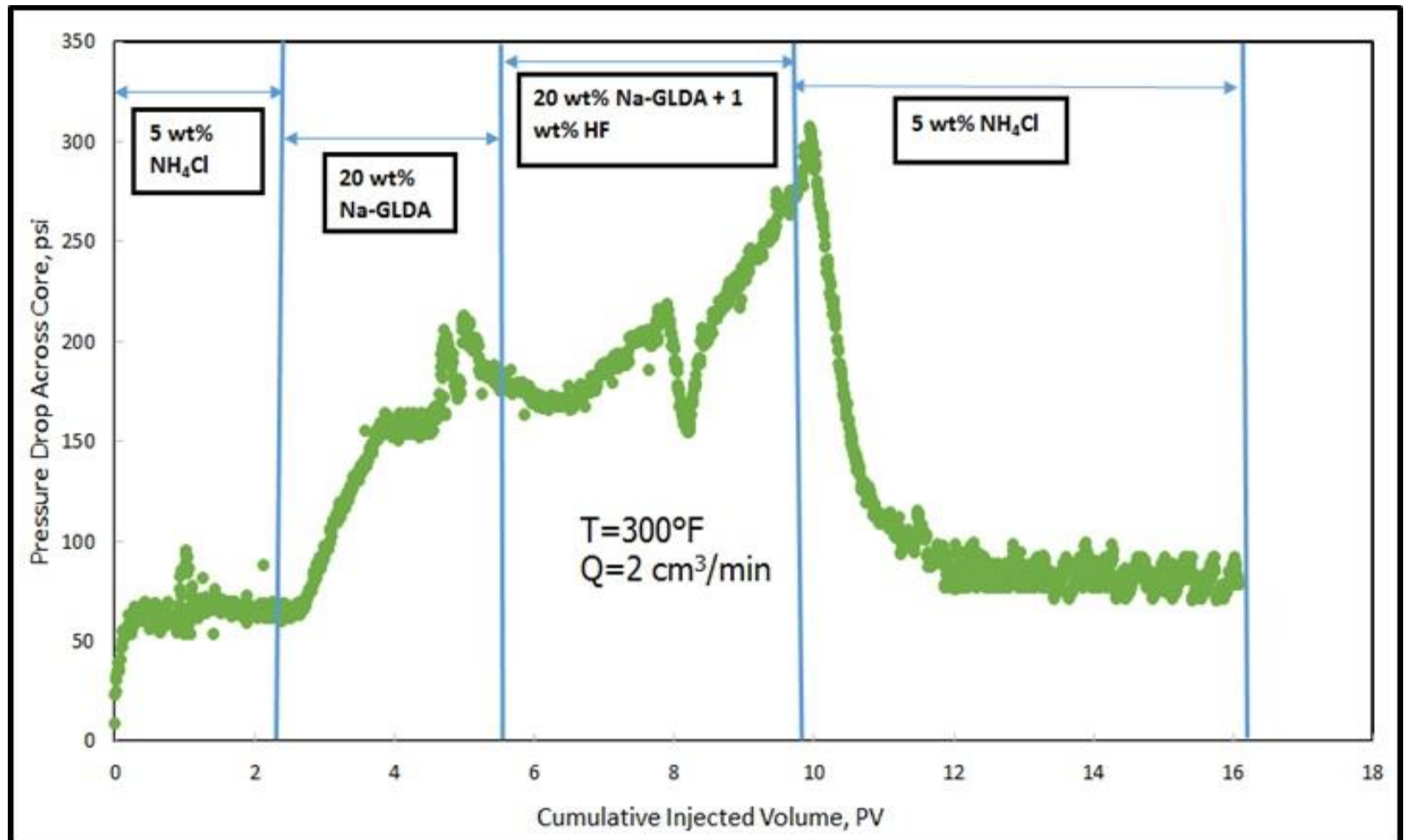


Figure 17. Pressure Drop Graph Bandera

As seen in Figure 17, the primary preflush of 5 wt% NH_4Cl was injected till about 2.5 PV till the core pressure drop stabilized, at which point the accumulator for 20 wt% Na-GLDA was activated, pumping the secondary preflush till about 5.6 PV. Following this the main acid mixture of 20 wt% Na-GLDA + 1 wt% HF was injected till approximately 9.8 PV. After this point, the postflush of 5 wt% NH_4Cl was injected till the core pressure drop stabilized. From the graph it is clear that once the secondary preflush is injected the pressure drop increases, this is due to a higher viscosity fluid entering the core. The pressure buildup continues further till about 5 PV, at which point there is a decrease in pressure drop. This drop could be due to opening on pore throats due to dissolution of ions specifically calcium. This pressure continues to drop through the initial injection phase of the main acid mixture, but the pressure drop starts to increase at about 6.5 PV due to pore blockage via precipitation. The pressure drop decreases rapidly at about 8 PV suggesting further dissolution of actions and possible chelation as well.

At 8.3 PV there pressure drop starts to increase again because of precipitation, which blocks pore throats and also due to possible fines migration. This steady increase could be due to some pH fluctuations which can cause aluminum fluorides to precipitate as well as silica gel. Once the postflush injection begins the graph shows a steady decline in pressure drop due to the injection of a lower viscosity ammonium chloride, and also due to further clearing of pore throats by movement of already dissolved or chelated ions to the outlet of the core holder. The pressure drop behavior for the Bandera core looks more random and problematic due to the nature of Bandera cores compared to

Berea cores. Bandera cores are much tighter cores with more illite, which is a migrating clay that blocks pore throats. Now we will analyze the ICP results.

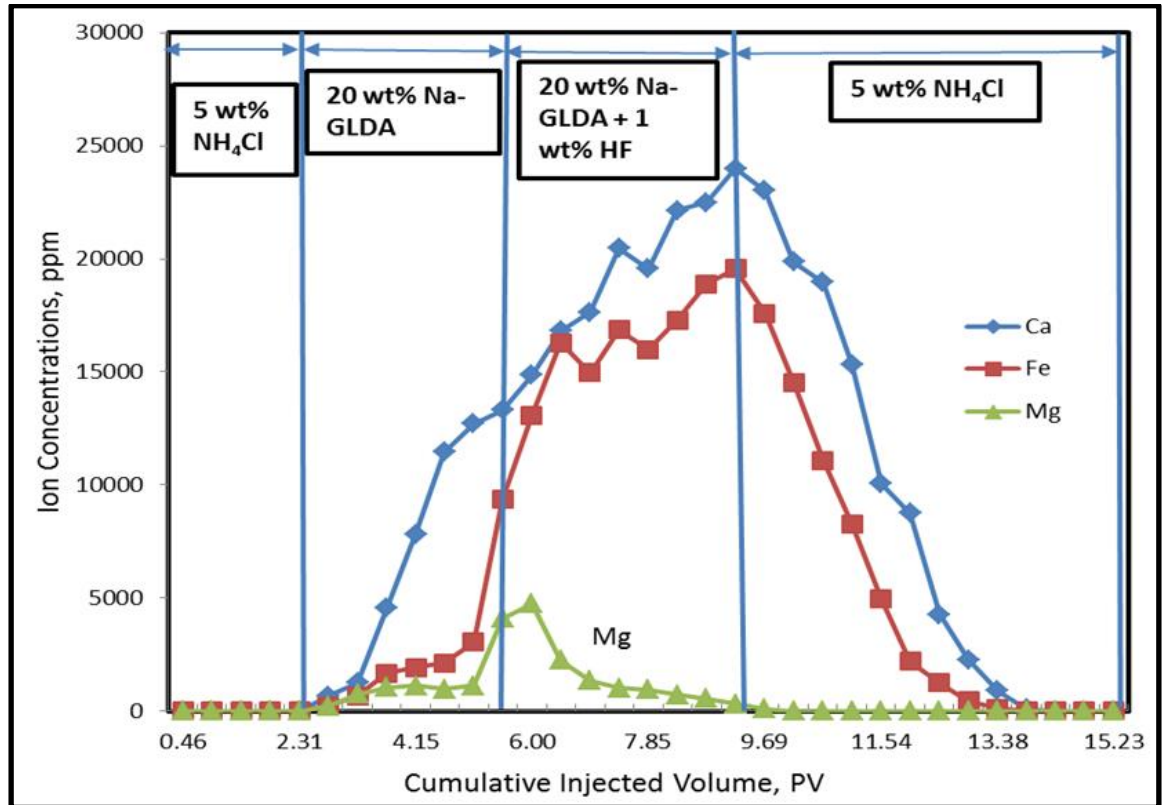


Figure 18. ICP Results Bandera

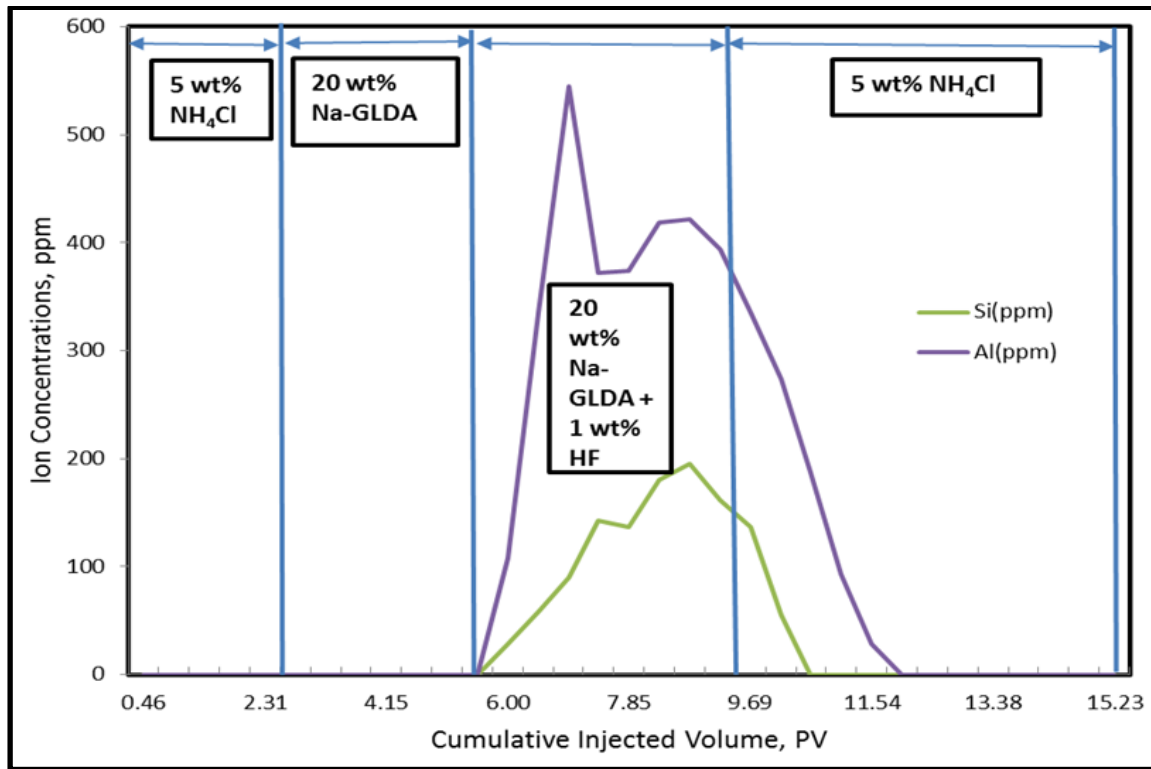


Figure 19. ICP Results Aluminum and Silicon Dissolution Bandera

Similar to the Berea case, we see that magnesium, aluminum and calcium were dissolved and chelated in high concentrations compared to aluminum and silicon. The reason for this behavior has been explained in the Berea analysis section. From the results it is clear once again that using Na-GLDA along with HF can help dissolve and chelate ions such as iron, calcium and magnesium, but its leaching action against aluminosilicates needs to be re-evaluated and studied further.

In order to explain this lack of aluminosilicate dissolution in both cores, an additional literature review was completed to explain the results. After carefully reading research papers by Mahmoud et al. 2011 and Gdanski 1999, it was found that, at high

temperatures, secondary and tertiary reactions between HF and aluminosilicates can cause precipitates to form including fluosilicates, fluoride salts and silica gel. Similar results were observed by a co-worker, Noble George, whose results are not published yet. He found excessive precipitate formation when using 20 wt% Na-GLDA and 1 wt% HF for clay dissolution experiments.

Secondary reactions between fluosilic acid and aluminosilicates results in the formation of Silica gel from the reaction (Gdanski 1999). This could prove why very little Si was found in ICP results because it precipitated in the core as silica gel. George's clay dissolution work also supports this theory as he found silica gel precipitate in his SEM analysis of reaction residue with 20 w% Na-GLDA + 1 wt% HF.

Tertiary reactions between HF and aluminosilicates can also cause the formation of another precipitate, which is Na_2SiF_6 . Mahmoud et al. suggests that this is formed when Na reacts with fluosilic acid. This precipitate is also found in George's research work when he reacted 20 wt% Na-GLDA + 1 wt% HF with clays. Lastly, another reaction product for tertiary and secondary reactions is aluminum fluoride species. This explains the low concentration of Al in the ICP samples because the various Al_xF_y could have precipitated within the core.

CHAPTER V

CONCLUSIONS

This study evaluated the use of two different chelating agents for specific purposes with regards to sandstone acidizing. In Chapter III, Citric acid was added to regular 9:1 mud acid to run clay dissolution experiments in order to overcome the problems faced with regular 9:1 mud acid. In particular, the problem of precipitation was addressed, and citric acid was added to mud acid in order to keep some of the damaging salts and ions from precipitating out of solution. The results suggest that adding 1 wt% citric acid to 9:1 mud acid provided the optimum results, both in terms of maximum dissolution of clays as well as minimizing precipitate formation. But, in comparison regular 9:1 mud acid by itself performed almost as well, suggesting that the addition of citric acid might not be required. This is because the cost of citric acid is considerable more than HCl or HF, and from a financial standpoint, it might not be viable even though experimentally it has been proven to provide better results.

Chapter IV looked into the use of a novel eco-friendly chelating agent, L-Glutamic acid N,N-Diacetic Acid or Na-GLDA. This recently developed chemical had been successfully tested with carbonate reservoirs, and its application was being extended to sandstone reservoirs as well. Apart from being eco-friendly, it is a thermally stable chemical at high temperatures, and has very low toxicity compared to other chelating agents such as HEDTA, NTP, EDTA etc. Before Na-GLDA could be tested with sandstone cores, a compatibility study with HF was completed to estimate the

optimum acid mixture formulation, and to also check for any incompatibilities between Na-GLDA and HF. The compatibility study revealed that the optimum acid mixture formulation was 20 wt% Na-GLDA + 1 wt% HF. It was also noted that at certain concentrations of both Na-GLDA and HF, a white hygroscopic precipitate was seen. This was later analyzed to be a fluoride salt of sodium, possibly NaHF_2 . Following the compatibility studies coreflood experiments were completed and the results suggested that Na-GLDA and HF together can dissolve calcium, iron and magnesium with ease but there are complication with aluminosilicate dissolution. It is possible that Na-GLDA and HF successfully leached aluminosilicates from the cores, but certain changes in pH or live acid concentration caused the aluminum and silicon to precipitate as aluminum fluoride salts, sodium hexafluosilicate and silica gel. Therefore the coreflood results were inconclusive as far as aluminosilicate dissolution is concerned, but it clearly showed that Na-GLDA can be used as a preflush to dissolve calcium, iron and magnesium, and prevent these cations from precipitating as harmful salts.

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